Appendix 3. Model Archive Summary for Nitrate Plus Nitrite Concentration at U.S. Geological Survey Station 07144780, North Fork Ninnescah River above Cheney Reservoir, Kansas, during November 14, 2015, through September 30, 2021

This model archive summary summarizes the nitrate plus nitrite (NO_3NO_2) concentration model developed to compute 15-minute, hourly, or daily nitrate plus nitrite concentrations during November 14, 2015, onward. This model supersedes all prior models used during this period. The methods follow U.S. Geological Survey (USGS) guidance as referenced in relevant Office of Surface Water/Office of Water Quality Technical Memoranda and USGS Techniques and Methods, book 3, chapter C4 (Rasmussen and others, 2009; U.S. Geological Survey, 2016).

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Site and Model Information

Site number: 07144780

Site name: North Fork Ninnescah River above Cheney Reservoir, Kansas

Location: Lat 37°51'45", long 98°00'49" referenced to North American Datum of 1927, in NE 1/4 SE 1/4 NE 1/4 sec.19, T.25 S., R.6 W., Reno County, Kans., hydrologic unit 11030014, on right bank at upstream side of county highway bridge, 10 miles south of Hutchinson, 18.1 miles upstream from Cheney Dam.

Equipment: A YSI, Inc., EXO water-quality monitor (YSI, Inc., 2017) equipped with sensors for water temperature, specific conductance, dissolved oxygen, pH, and turbidity was installed November 14, 2015. The EXO monitor was installed in a 4-inch-diameter metal or polyvinyl chloride (or PVC) pipe suspended from the downstream side of the bridge in the deepest, fastest flowing water. Measurements from the EXO were recorded every 15 minutes to hourly and transmitted hourly via satellite. Real-time stage was measured using a Design Analysis Water Log H–350/355 nonsubmersible pressure transducer.

Date model was created: August 9, 2022

Model calibration data period: November 25, 2015, through August 12, 2021 (dataset consisted of 44 discrete water-quality samples).

Model application date: November 14, 2015, onward (date of EXO continuous water-quality monitor installation).

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Model Calibration Dataset

All data were collected using USGS protocols (U.S. Geological Survey, 2006; Wagner and others, 2006; Bennett and others, 2014) and are stored in the USGS National Water Information System database (https://doi.org/10.5066/F7P55KJN; U.S. Geological Survey, 2022). Potential explanatory variables evaluated individually and in combination were water temperature, specific conductance, pH, dissolved oxygen, turbidity, seasonality (sine and cosine variables), and streamflow.

The regression model is based on 44 concomitant values of discretely collected nitrate plus nitrite concentration and continuously measured streamflow and water temperature during November 25, 2015, through August 12, 2021. Discrete samples were collected throughout the range of continuously observed hydrologic conditions. No samples had nitrate plus nitrite concentrations that were less than laboratory minimum reporting level. All potential explanatory variables were time interpolated within the 15-minute to hourly continuous record based on the discrete sample time. The maximum time span between two continuous data points used for interpolation was 4 hours (to preserve the sample dataset, field monitor averages obtained during sample collection were used for model development data if no continuous data were available or if gaps larger than 4 hours in the continuous data record resulted in missing interpolated data). Summary statistics and the complete model-calibration dataset are provided below. Potential outliers were identified using the methods described in Rasmussen and others (2009) and Helsel and others (2020). All potential outliers were investigated by reviewing sample collection information sheets and laboratory reports; if there were no clear issues, explanations, or conditions that would cause a result to be invalid for model calibration, the sample was retained in the dataset. Two samples in the model calibration dataset were flagged as outliers but were retained in the dataset after further review.

Nitrate plus Nitrite Sampling Details

Discrete water-quality samples were collected over a range of hydrologic conditions primarily using a combination of equal depth- and width-integrated and multiple-vertical sample collection techniques (U.S. Geological Survey, 2006). Equal-width-increment and multiple-vertical sample cross sections included five to 12 sampling points with more than 85 percent of samples including 10 or more sampling points. Samples were collected either instream as a wading sample within 300 feet of the bridge or from the downstream side of the bridge using a Federal Interagency Sedimentation Project depth-integrated sampler with a polytetrafluoroethylene bottle, cap, and nozzle. Discrete samples were collected on a semifixed to event-based schedule two to 11 times per year. Samples were analyzed for nitrate plus nitrite by the Wichita Municipal Water and Wastewater Laboratory in Wichita, Kans., according to standard methods (Eaton and others, 1995).

Continuous Water-Quality Data

Water temperature was continuously measured (15 minutes to hourly) using a YSI, Inc., EXO multiparameter sonde (YSI, Inc., 2017). The water-quality monitor was operated and maintained according to standard USGS methods (Wagner and others, 2006; Bennett and others, 2014). Discharge was computed using a nonsubmersible pressure transducer following standard USGS methods (Turnipseed and Sauer, 2010; Painter and Loving, 2015). All continuous water-quality

data at the North Fork Ninnescah River above Cheney Reservoir are available in near-real time (updated hourly) from the USGS National Water Information System database (https://doi.org/10.5066/F7P55KJN; U.S. Geological Survey, 2022) using the site number 07144780.

Model Development

Ordinary least squares linear regression was used to develop surrogate regression models that relate continuous water-quality conditions to discretely sampled constituent concentrations. All regressions were computed using the R software environment (R Core Team, 2020). The data and subsequent regression equation must meet the five assumptions necessary to apply ordinary least squares regression: the dependent variable is linearly related to the explanatory variables, data used to fit the model are representative of the data of interest, the variance of the residuals is constant (homoscedastic), the residuals are independent of the explanatory variables, and the residuals are normally distributed (Helsel and others, 2020). Previously published explanatory variables also were considered for continuity.

Water temperature and streamflow were selected as a good surrogate for nitrate plus nitrite concentration based on residual plots, coefficient of determination (R^2), and model standard percentage error (MSPE). Values for the aforementioned statistics were computed and are included below along with all relevant sample data and additional statistical information.

Model Summary

Summary of final nitrate plus nitrite (NO_3NO_2) regression analysis at USGS site 07144780:

NO_3NO_2 concentration-based model:

$$NO_3NO_2 = -(0.388 \times \log_{10}(Q)) - (0.0554 \times TEMP) + 2.58,$$

where,

NO_3NO_2 = nitrate plus nitrite, in milligrams per liter as Nitrogen (mg/L as N) (USGS parameter code 00631);

Q = streamflow, instantaneous, cubic feet per second (ft^3/s) (USGS parameter code 00060);

$\log_{10}$ = decimal logarithm and

TEMP = water temperature, in degrees Celsius (°C) (USGS parameter code 00010)

Extrapolation, defined as computation beyond the range of the model calibration dataset, may be no more than 10 percent outside the range of the calibration data used to fit the model and is therefore limited. The extrapolation limit for nitrate plus nitrite concentration using this model is 2.574 milligrams per liter as N. Computed estimates outside that limit are not supported by the current model calibration dataset.

Model Statistics, Data, and Plots

Definitions

Variable	Explanation
Cook's D	Cook's distance, a measure of influence (Helsel and others, 2020)
DFFITS	Difference in fits, a measure of influence (Helsel and others, 2020)
E.vars	Explanatory variables
Leverage	An outlier's measure in the x direction (Helsel and others, 2020)
LOESS	Local polynomial regression fitting (Helsel and others, 2020)
logQ	Streamflow, instantaneous, cubic feet per second (ft^3/s) (USGS parameter code 00060), $\log_{10}$ transformed
MSE	Model standard error (Helsel and others, 2020)
MSPE	Model standard percentage error (Helsel and others, 2020)
NO3NO2	Inorganic nitrogen (nitrate plus nitrite), in milligrams per liter (mg/L) as N (USGS parameter code 00631)
Pr(>|*t*|)	The probability that the independent variable has no effect on the dependent variable (Helsel and others, 2020)
RMSE	Root mean square error (Helsel and others, 2020)
TEMP	Water temperature, in degrees Celsius (°C) (USGS parameter code 00010)
t value	Student's *t* value; the coefficient divided by its associated standard error (Helsel and others, 2020)

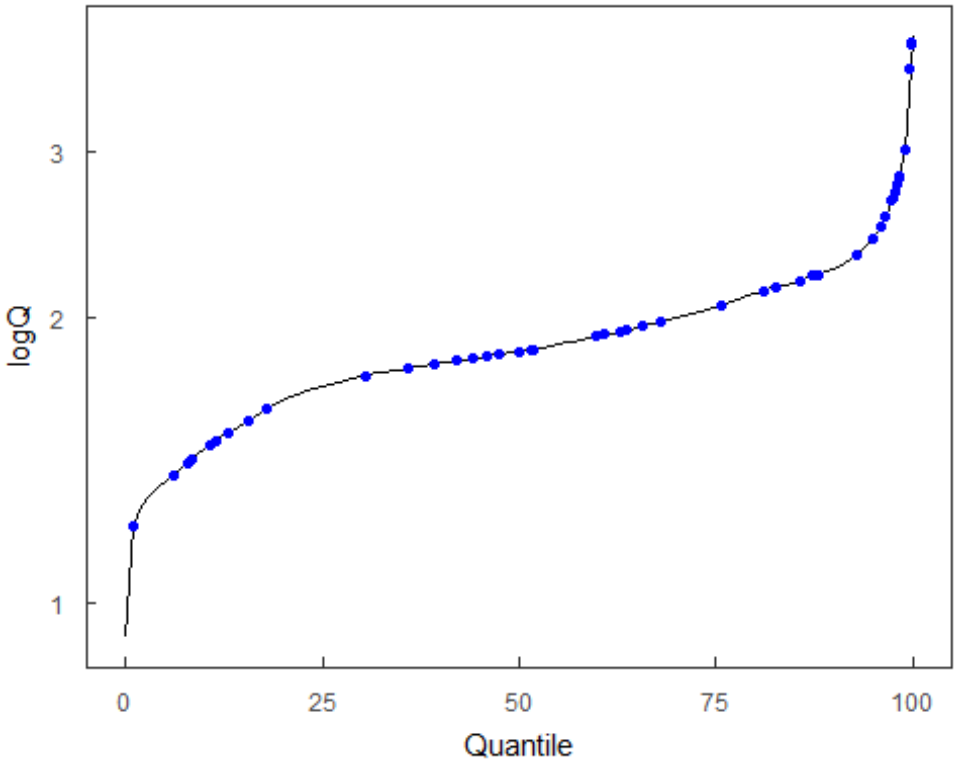
Model

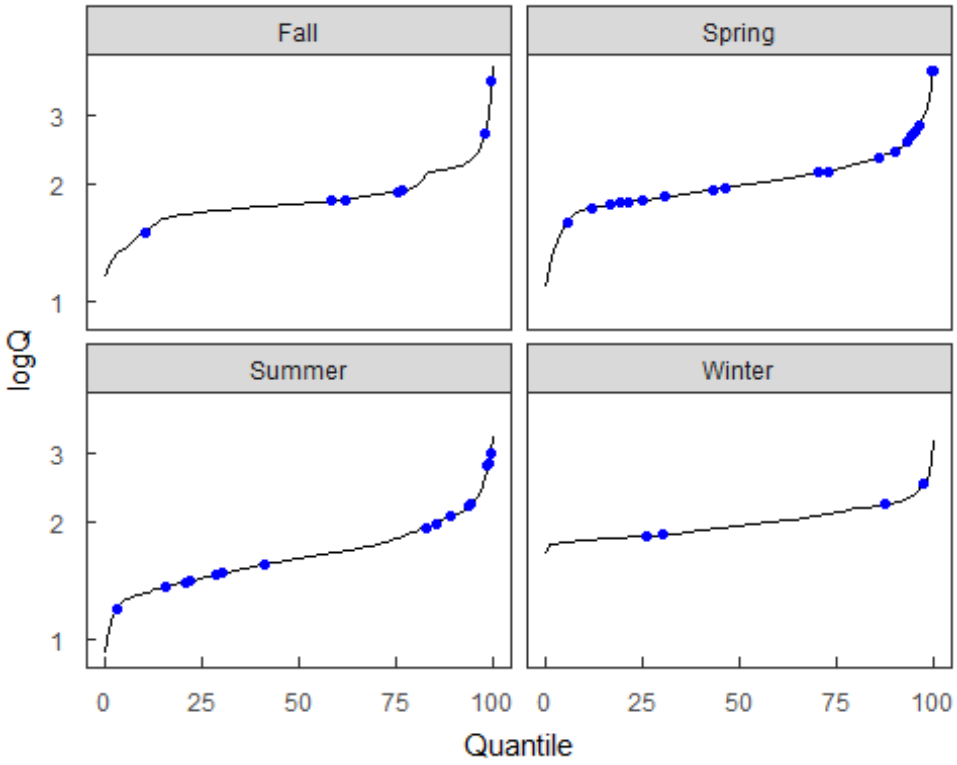
$$NO_3NO_2 = -(0.388 \times \log_{10}(Q)) - (0.0554 \times TEMP) + 2.58$$

Variable summary statistics

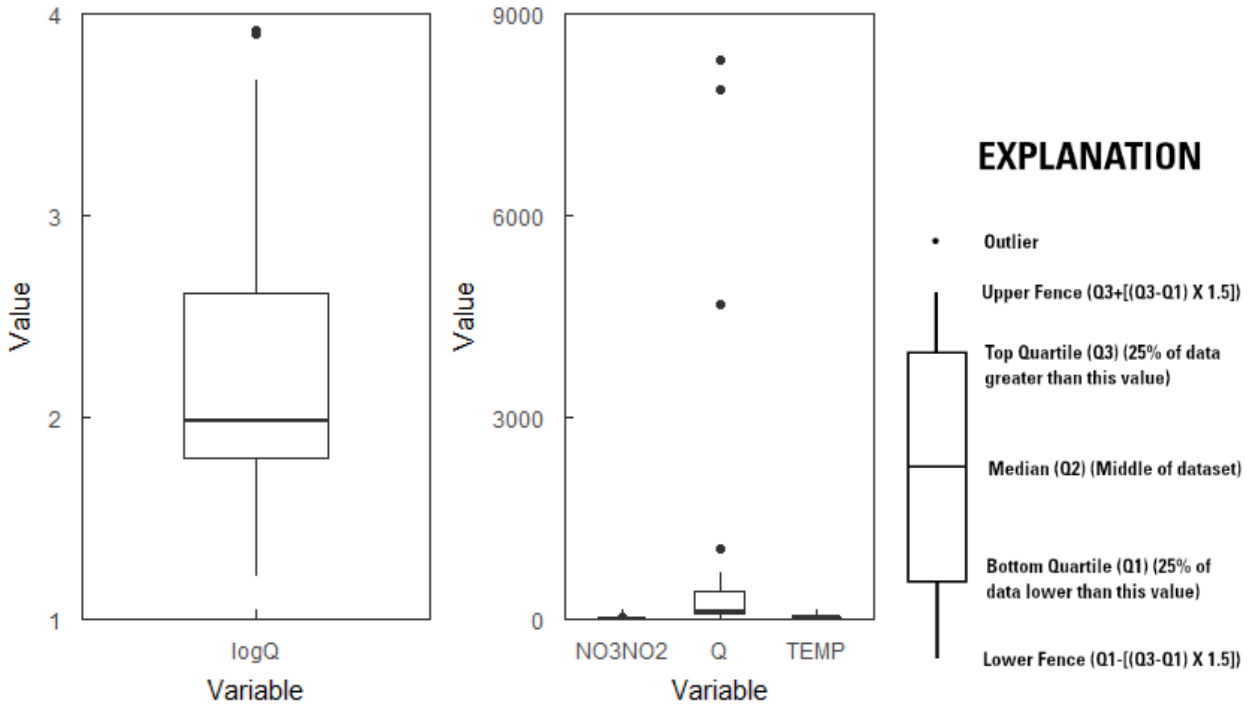
Variable	Minimum	Q1	Median	Mean	Q3	Maximum
logQ	1.21	1.8	1.97	2.19	2.61	3.92
NO3NO2	0.08	0.28	0.61	0.754	1.09	2.34
Q	16	62.5	94.4	673	411	8290
TEMP	0.373	11.3	17.9	17.7	24.3	33.6

Duration plots

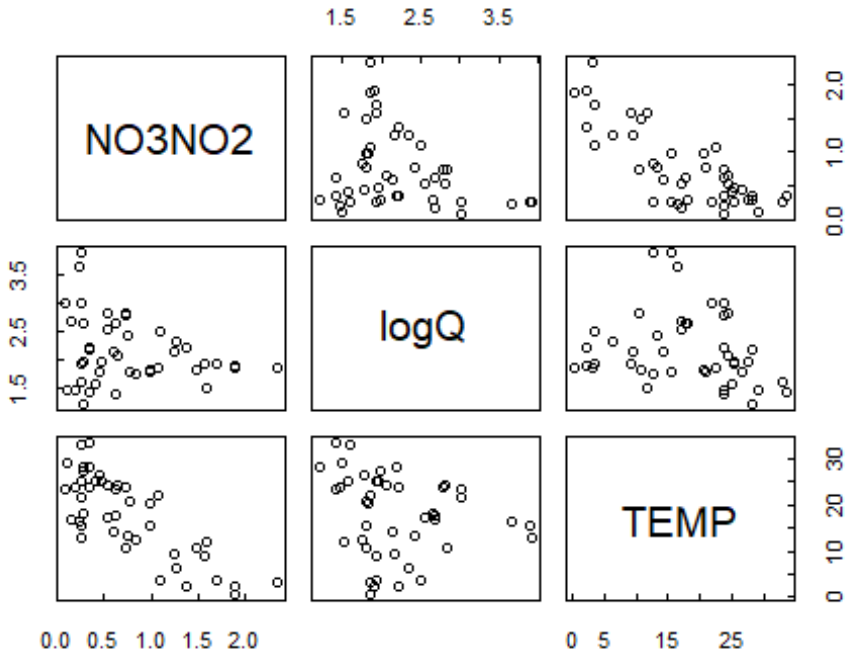




Box plots



Scatter plots



The x- and y-axis labels for a given bivariate plot are defined by the intersecting row and column labels.

Basic model statistics

Statistic	Value
Observations	44
R^2	0.804
Adjusted R^2	0.794
RMSE	0.257
Upper MSPE (90%)	34.1
Lower MSPE (90%)	-34.1

Model coefficients

	Estimate	Standard error	t value	Pr(>|t|)
(Intercept)	2.5824624	0.1745816	14.792290	0e+00
logQ	-0.3876787	0.0622011	-6.232667	2e-07
TEMP	-0.0554387	0.0044940	-12.336080	0e+00

Correlation matrix

	NO3NO2	logQ	TEMP
NO3NO2	1.0000000	-0.2737034	-0.7858984
logQ	-0.2737034	1.0000000	-0.1904888
TEMP	-0.7858984	-0.1904888	1.0000000

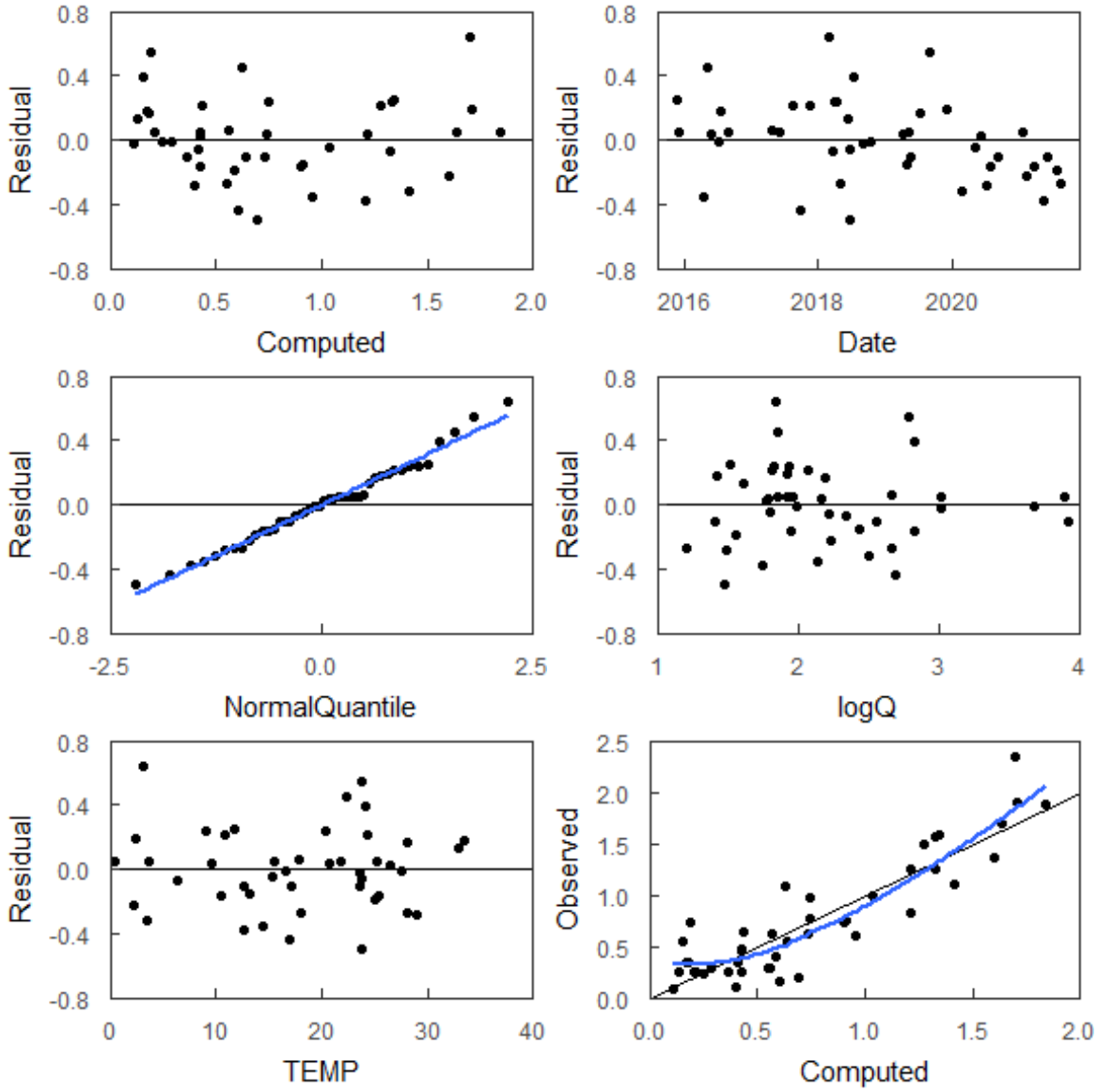
Outlier test criteria

Leverage	DFFITS	CooksD
0.2045	0.5222	0.263

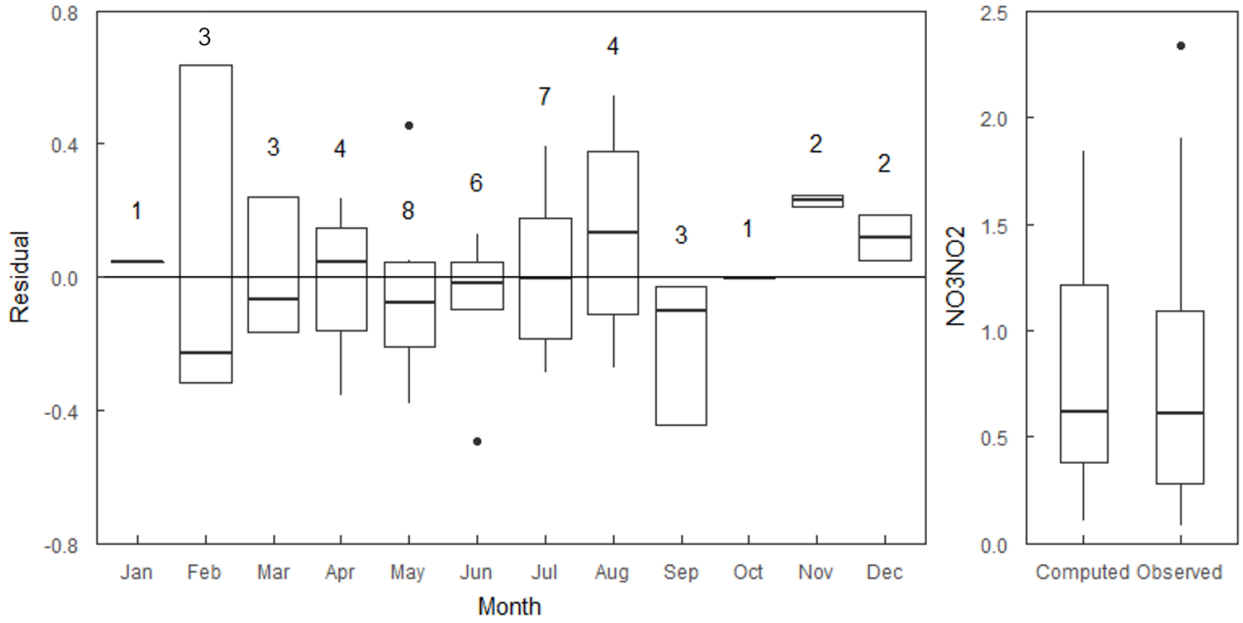
Flagged observations

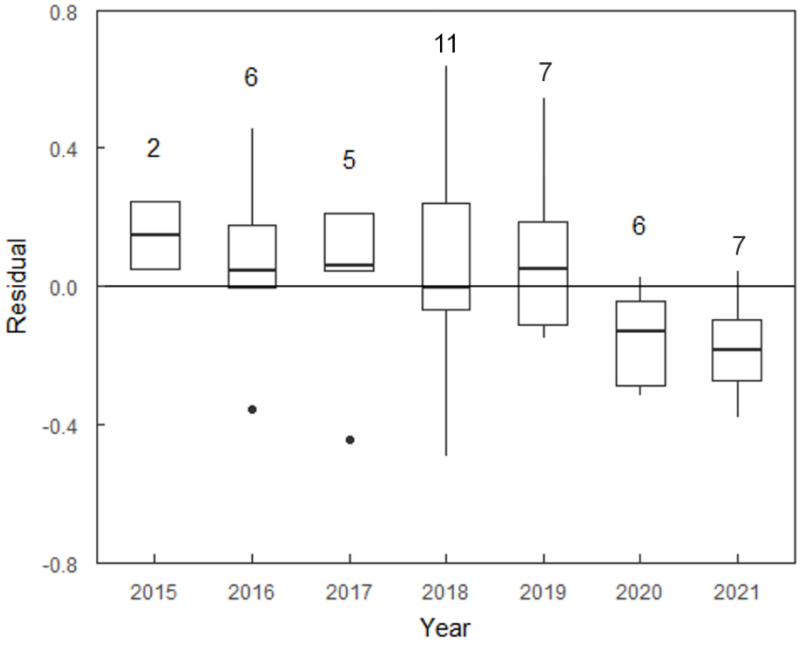
datetime	NO3NO2	CooksD	DFFITS	Leverage	Studentized Residual
2018-02-23 15:00:00	2.34	0.266	0.969	0.104	2.85
2019-08-26 11:30:00	0.73	0.102	0.581	0.0603	2.29

Statistical plots



The blue line shows the locally estimated scatterplot smoothing (LOESS). The black dots correspond to observed values. The black line represents the 1:1 line.





EXPLANATION

7 Number of values

Outlier

Upper Fence (Q3+[(Q3-Q1) X 1.5])

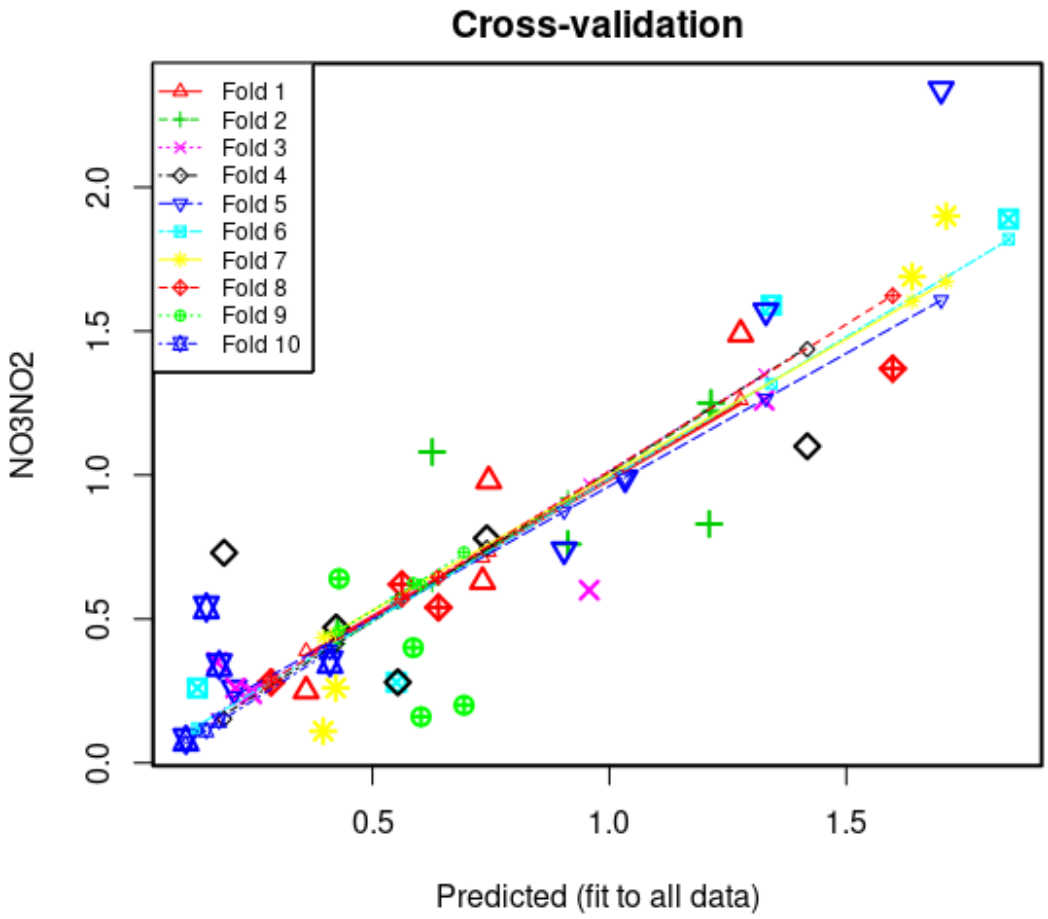
Top Quartile (Q3) (25% of data greater than this value)

Median (Q2) (Middle of dataset)

Bottom Quartile (Q1) (25% of data lower than this value)

Lower Fence (Q1-[(Q3-Q1) X 1.5])

Cross Validation



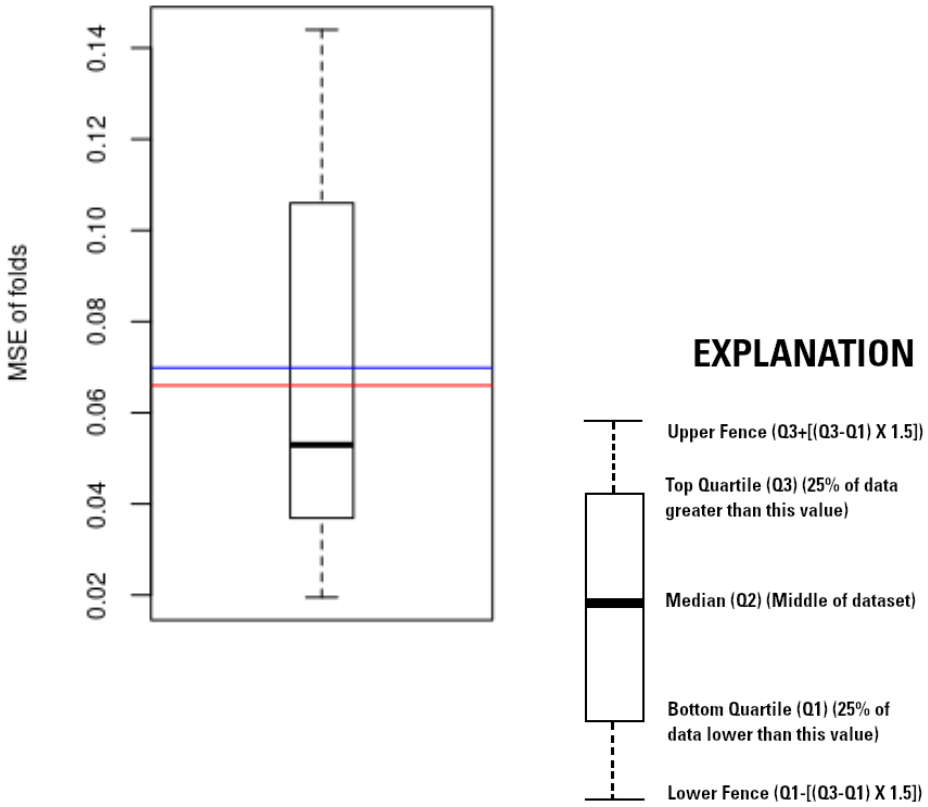
Fold - equal partition of the data (10 percent of the data).

Large symbols – observed value of a data point removed in a fold.

Small symbols – recomputed value of a data point removed in a fold.

Recomputed regression lines – adjusted regression line with one fold removed.

Statistic	Value
Minimum MSE of folds	0.0195
Median MSE of folds	0.0530
Mean MSE of folds	0.0698
Maximum MSE of folds	0.144
(Mean MSE of folds) / (Model MSE)	1.0600



Red line - Model MSE

Blue line - Mean MSE of folds

Model calibration dataset

datetime	NO3NO2	logQ	TEMP	Computed
2015-11-25 11:00:00	1.59	1.51	11.8	1.34
2015-12-01 12:10:00	1.69	1.92	3.58	1.64
2016-04-19 10:25:00	0.6	2.14	14.4	0.957
2016-05-11 12:10:00	1.08	1.85	22.3	0.626
2016-05-24 09:30:00	0.78	1.79	20.7	0.741
2016-07-08 10:35:00	0.28	1.99	27.5	0.286
2016-07-22 13:30:00	0.35	1.42	33.6	0.172
2016-08-31 10:45:00	0.26	3.01	21.8	0.208
2017-04-20 12:00:00	0.62	2.67	17.8	0.562
2017-06-07 11:30:00	0.47	1.96	25.2	0.423
2017-08-11 11:00:00	0.64	2.07	24.4	0.43

datetime	NO3NO2	logQ	TEMP	Computed
2017-09-28 10:30:00	0.16	2.69	16.9	0.602
2017-11-16 13:50:00	1.49	1.81	10.9	1.28
2018-02-23 15:00:00	2.34	1.84	3.02	1.7
2018-03-20 10:30:00	1.26	2.34	6.31	1.33
2018-03-30 10:40:00	1.57	1.94	9.05	1.33
2018-04-13 12:30:00	0.98	1.82	20.4	0.745
2018-05-04 10:00:00	0.28	2.66	18	0.551
2018-06-08 14:20:00	0.26	1.6	33	0.131
2018-06-21 10:10:00	0.2	1.47	23.8	0.693
2018-06-26 13:20:00	0.35	2.22	23.7	0.41
2018-07-14 12:00:00	0.54	2.82	24.2	0.15
2018-09-05 09:55:00	0.08	3.01	23.6	0.106
2018-10-09 10:10:00	0.24	3.67	16.5	0.245
2019-04-02 10:50:00	1.25	2.16	9.57	1.21
2019-05-02 11:20:00	0.76	2.43	13.1	0.912
2019-05-08 12:00:00	0.26	3.9	15.5	0.211
2019-05-21 12:30:00	0.25	3.92	12.7	0.36
2019-07-08 11:30:00	0.34	2.19	28.1	0.177
2019-08-26 11:30:00	0.73	2.78	23.8	0.187
2019-12-03 10:20:00	1.9	1.91	2.33	1.71
2020-02-26 10:30:00	1.1	2.5	3.52	1.42
2020-05-07 10:30:00	0.99	1.8	15.3	1.03
2020-06-04 10:20:00	0.45	1.77	26.5	0.426
2020-07-08 11:00:00	0.11	1.48	29.1	0.396
2020-07-21 10:10:00	0.26	1.94	25.4	0.423
2020-09-03 10:20:00	0.63	1.4	23.6	0.732
2021-01-12 10:10:00	1.89	1.86	0.373	1.84
2021-02-01 11:00:00	1.37	2.23	2.19	1.6
2021-03-23 11:40:00	0.74	2.83	10.5	0.904
2021-05-10 10:50:00	0.83	1.74	12.6	1.21
2021-06-01 10:40:00	0.54	2.56	17.2	0.639
2021-07-22 10:40:00	0.4	1.56	25.1	0.586
2021-08-12 11:00:00	0.28	1.21	28.2	0.554

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